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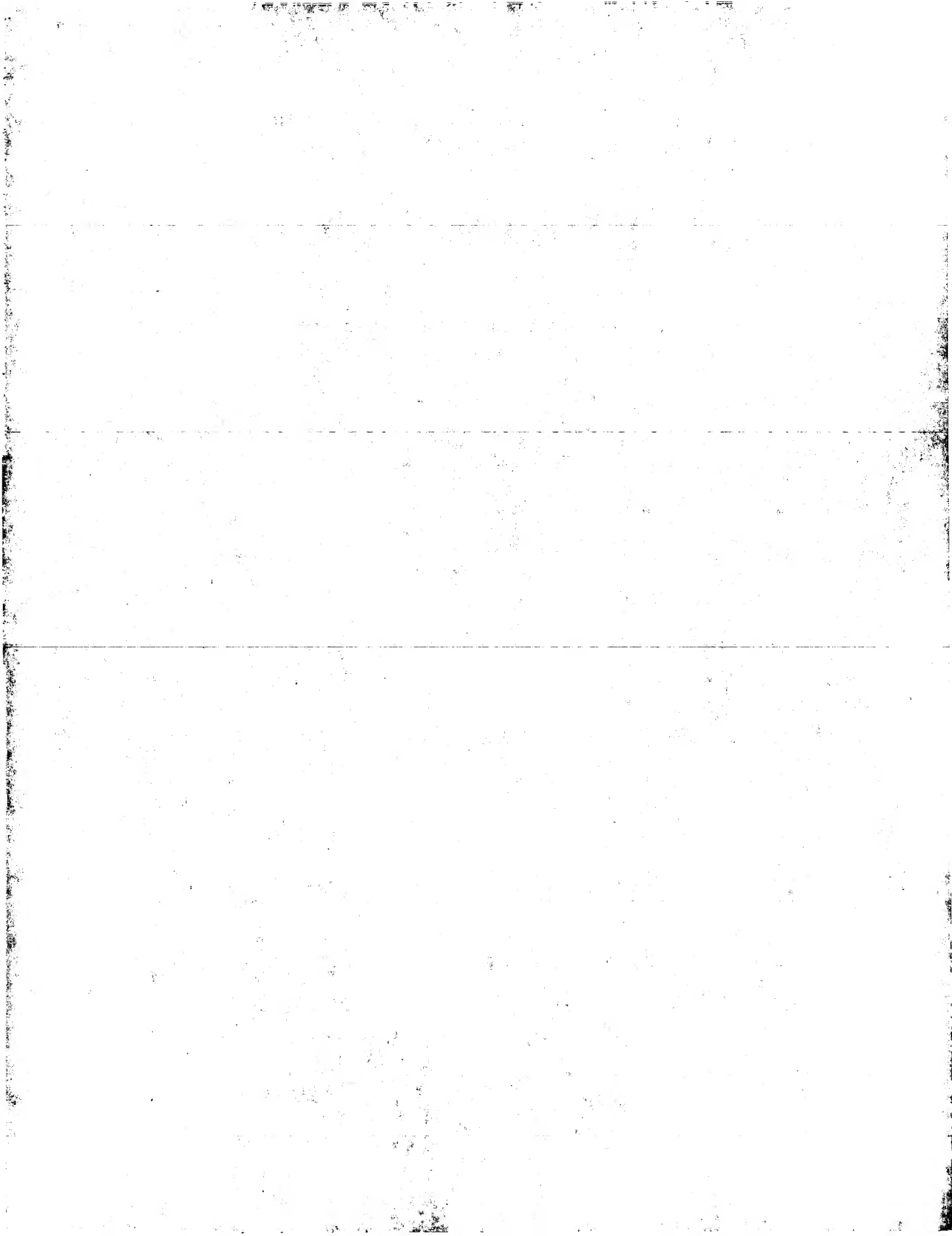
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(54) **Controlled sudsing detergent compositions.**

(57) Built granular detergent compositions having high sudsing properties in cool e.g. hand washing conditions and suppressed sudsing in hotter machine washing conditions comprise an organic detergent component containing at least 50% by weight of nonionic and/or water-soluble cationic surfactants, detergency builders, and a ternary suds controlling system which is a uniform dispersion of hydrophobic silica, and a hydrophilic nonionic dispersant in wax.

EP 0 008 829 A1

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CONTROLLED SUDSING DETERGENT COMPOSITIONS

Granular detergent compositions, particularly those intended for domestic clothes washing, are employed in a wide range of washing conditions. Some garments are washed by hand, at temperatures ranging from nearly cold up to about 45-50°C, some are washed in upright washing machines, some in the more modern drum machines at temperatures ranging from cold to 40°C, 60°C and near boiling according to the machine wash cycle selected. As the user naturally prefers to be able to use a single washing product for all purposes, it is necessary to design products which have good performance in all washing conditions. The sudsing properties of detergent compositions are very important features of their performance. Thus users expect a considerable degree of sudsing when they use the products for hand washing, i.e. at low temperatures with relatively mild agitation. On the other hand, in drum washing machines, very little suds formation can be tolerated at any temperature, since excessive suds interfere with the action of the wash liquor on the clothes, and may even overflow from the machine. This requirement is opposed to the natural tendency of detergent compositions to form suds more copiously in the conditions of the hotter wash cycles of a drum washing machine than in the cool hand washing conditions.

Many formulations have been made which achieve suds suppression in drum washing machines with reasonable success, and some attempts have been made to obtain also

- 5
- (A) from 3% to 30% preferably 5 to 15% of organic detergent which detergent contains at least 50% by weight thereof of nonionic and/or water-soluble cationic surfactant;
- (B) from 10% to 96.9% preferably 20% to 60% of detergency builder; and
- (C) as suds controlling system, from 0.1% to 5% of a dispersion containing by weight thereof
- 10 (a) from 5% to 50%, preferably from 5% to 15%, of a hydrophilic nonionic dispersing agent having an HLB in the range from 14 to 19, and
- (b) from 5% to 55%, preferably from 5% to 15%, of hydrophobic silica, uniformly dispersed in
- 15 (c) from 40% to 90%, preferably from 60% to 85% of wax;

Wherein the suds-controlling system is in admixture with preformed granules comprising some or all of the organic detergent and/or detergency builder components of the composition.

20 DETAILED DESCRIPTION OF THE INVENTION

THE ORGANIC DETERGENT

The organic detergent component of the compositions of the invention consists of at least 50% by weight of nonionic and/or water-soluble cationic surfactants and may additionally

25 contain anionic, zwitterionic and amphoteric surfactants. Detergent compositions based upon predominantly anionic organic detergents when containing the ternary suds controlling systems of the invention tend to over-suds in drum washing machines at low or moderate temperature. Preferred

30 organic detergent mixtures comprises 35% to 99% of nonionic surfactants, of the types described more fully hereinafter. A more preferred organic detergent mixture comprises a water-soluble or water-dispersible combination of ethoxylated nonionic, water-soluble quaternary ammonium cationic, and

35 anionic surfactants wherein the weight ratio of anionic to

adequate sudsing at low temperatures, but these methods and compositions therefor are generally effective only in detergent compositions based upon certain organic detergents.

5 It has recently been found that built laundry detergents based upon specific mixtures of selected anionic, nonionic and cationic surfactants have improved cleaning properties for removing greasy and oily stains, without detriment to their effectiveness for removing
10 particulate soiling or for soil suspension or whiteness maintenance. To achieve the desired pattern of sudsing with detergent compositions based upon these organic detergent mixtures has proved very difficult. Previously
15 known suds depressants such as high molecular weight soaps or fatty acids, waxes, silicones and various known mixtures thereof, have failed in various ways, for instance in giving insufficient suppression of sudsing in the boil wash cycles of drum washing machines, or in giving too much suds suppression under hand
20 washing conditions.

 It has now been found that certain combinations of wax, hydrophilic nonionic dispersant and hydrophobic silica provide the desired suds pattern with the above mentioned types of organic detergents, and with some
25 other organic detergents or mixtures thereof.

PRIOR ART

 There are very many patents and patent applications relating to suds controlling agents, and the following may be mentioned as typical: British Patents 1,021,098,
30 1,099,502, 1,207,777, 1,340,043, 1,407,997, 1,492,938, 1,492,939, British Patent Applications 75-11002, 76-26323.

SUMMARY OF THE INVENTION

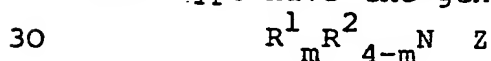
 According to the invention, there is provided a
35 granular built detergent composition having a controlled sudsing pattern characterised in that it comprises the following components, in per cent by weight:

cationic surfactant is no more than 5:1 and the weight ratio of nonionic to cationic surfactant is at least 2:3, and wherein the surfactant system contains anionic and cationic surfactants in an equivalent ratio of at least 1:1.

- 5 Mixtures of this sort are described in copending European Patent Application 78 200 050.9. In the preferred systems, the anionic and cationic surfactants have a combined total of no more than 34 carbon atoms counted in hydrophobic groups having at least 4 consecutive carbon atoms (e.g. 10 alkyl, aryl, alkaryl, aralkyl groups etc.). In more preferred systems, the number of such hydrophobic group carbon atoms totals from about 18 to 33, especially from about 26 to 32, with the anionic surfactant providing at least 12 of the carbon atoms. These hydrophobicity limi- 15 tations have been found to optimize the interaction of the ternary active system with greasy and oily stains on fabrics and to correspond to compositions of maximum grease detergency effectiveness.

In these detergent systems, the cationic surfactant is 20 a water-soluble quaternary ammonium compound having a critical micelle concentration for the pure material of at least 200 p.p.m. and preferably at least 500 p.p.m. specified at 30°C and in distilled water. Literature values are taken where possible, especially surface tension or 25 conductimetric values - see Critical Micelle Concentrations of Aqueous Surfactant System, P. Mukerjee and K.J. Mysels, NSRDS - NBS 36 (1971).

A highly preferred group of cationic surfactants of this type have the general formula:



wherein R^1 is selected from C_8 - C_{20} alkyl, alkenyl and alkaryl groups; R^2 is selected from C_1 - C_4 alkyl and benzyl groups; Z is an anion in number to give electrical neutrality; and m is 1, 2 or 3; provided that when m is 2 R^1 has less than 35 carbon atoms and when m is 3, R^1 has less than 9 carbon atoms.

Where m is equal to 1, it is preferred that R^2 is a methyl group. Preferred compositions of this mono-long chain type include those in which R^1 is a C_{10} to C_{16} alkyl group. Particularly preferred compositions of this class include C_{12} alkyl trimethylammonium halide and C_{14} alkyl trimethylammonium halide.

Where m is equal to 2, the R^1 chains should have less than 14 carbon atoms. Thus, ditallowdimethylammonium chloride and distearyldimethylammonium chloride, which are used conventionally as fabric softeners and static control agents in detergent compositions, may not be used as the cationic component in the surfactant mixtures of the present invention. Particularly preferred cationic materials of this class include di- C_8 alkyldimethylammonium halide and di- C_{10} alkyldimethylammonium halide materials.

Where m is equal to 3, the R^1 chains should be less than 9 carbon atoms in length. An example is trioctyl methyl ammonium chloride. The reason for this chain length restriction, as is also the case with the di-long chain cationics described above, is the relative insolubility of these tri- and di-long chain materials.

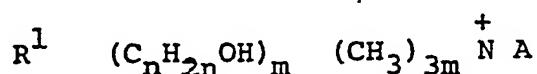
Another highly preferred group of cationic compounds have the general formula:

$R^1 R_m^2 R_m^3 N^{+} A$ wherein R^1 represents a C_{6-24} alkyl or alkenyl group or a C_{6-12} alkaryl group, each R^2 independently represents a $(C_n H_{2n} O)_x H$ group where n is 2, 3 or 4 and x is from 1 to 14, the sum total of $C_n H_{2n} O$ groups in R_m^2 being from 1 to 14, each R^3 independently represents a C_{1-12} alkyl or alkenyl group, an aryl group or a C_{1-6} alkaryl group, m is 1, 2 or 3, and A is an anion.

In this group of compounds, R^1 is selected from C_{6-24} alkyl or alkenyl groups and C_{6-12} alkaryl groups; R^3 is selected from C_{1-12} alkyl or alkenyl groups and

C_{1-6} alkaryl groups. When m is 2, however, it is preferred that the sum total of carbon atoms in R^1 and R^3_{3-m} is no more than about 20 with R^1 representing a C_{8-18} alkyl or alkenyl group. More preferably the sum total of carbon atoms in R^1 and R^3_{3-m} is no more than about 17 with R^1 representing a C_{10-16} alkyl or alkenyl group. When m is 1, it is again preferred that the sum total of carbon atoms in R^1 and R^3_{3-m} is no more than about 17 with R^1 representing a C_{10-16} alkyl or alkaryl group.

Additionally in this group of compounds, the total number of alkoxy radicals in polyalkoxy groups (R^2_m) directly attached to the cationic charge centre should be no more than 14. Preferably, the total number of such alkoxy groups is from 1 to 7 with each polyalkoxy group (R^2) independently containing from 1 to 7 alkoxy groups; more preferably, the total number of such alkoxy groups is from 1 to 5 with each polyalkoxy group (R^2) independently containing from 1 to 3 alkoxy groups. Especially preferred are cationic surfactants having the formula:



wherein R^1 is as defined immediately above, n is 2 or 3 and m is 1, 2 or 3.

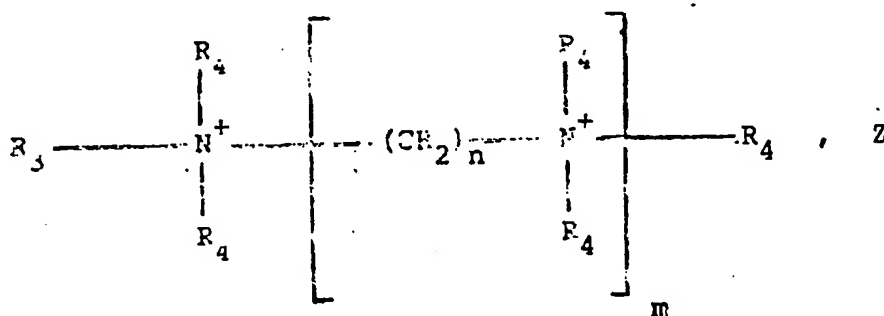
Particularly preferred cationic surfactants of the class having m equal to 1 are dodecyl dimethyl hydroxyethyl ammonium salts, dodecyl dimethyl hydroxypropyl ammonium salts, myristyl dimethyl hydroxyethyl ammonium salts and dodecyl dimethyl dioxyethylenyl ammonium salts. When m is equal to 2, particularly preferred cationic surfactants are dodecyl dihydroxyethyl methyl ammonium salts, dodecyl dihydroxypropyl methyl ammonium salts, dodecyl dihydroxyethyl ethyl ammonium salts, myristyl dihydroxyethyl methyl ammonium salts, cetyl dihydroxyethyl methyl ammonium salts, stearyl dihydroxyethyl methyl ammonium salts, oleyldi

hydroxyethyl methyl ammonium salts, and dodecyl hydroxyethyl hydroxypropyl methyl ammonium salts. When m is 3, particularly preferred cationic surfactants are dodecyl trihydroxyethyl ammonium salts, myristyl trihydroxyethyl ammonium salts, cetyl trihydroxyethyl ammonium salts, stearyl trihydroxyethyl ammonium salts, oleyl trihydroxyethyl ammonium salts, dodecyl dihydroxyethyl hydroxypropyl ammonium salts and dodecyl trihydroxy propyl ammonium salts.

In the above, the usual inorganic salt counterions can be employed, for example, chlorides, bromides and borates. Salt counterions can also be selected from organic acid anions, however, such as the anions derived from organic sulphonic acids and from sulphuric acid esters. A preferred example of an organic acid anion is a C₆₋₁₂ alkaryl sulphonate.

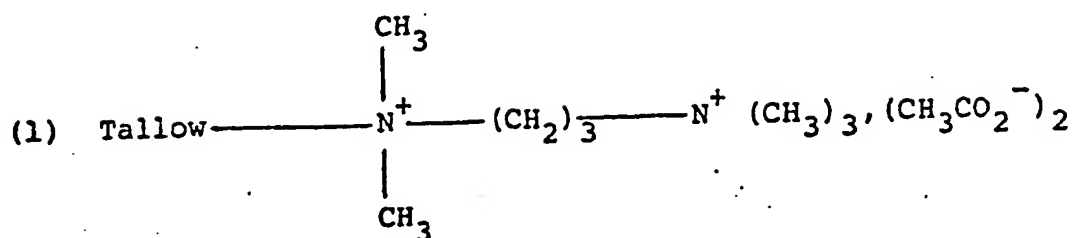
Of all the above cationic surfactants, especially preferred are dodecyl dimethyl hydroxyethyl ammonium salts and dodecyl dihydroxyethyl methyl ammonium salts.

Another group of useful cationic compounds are the polyammonium salts of the general formula:

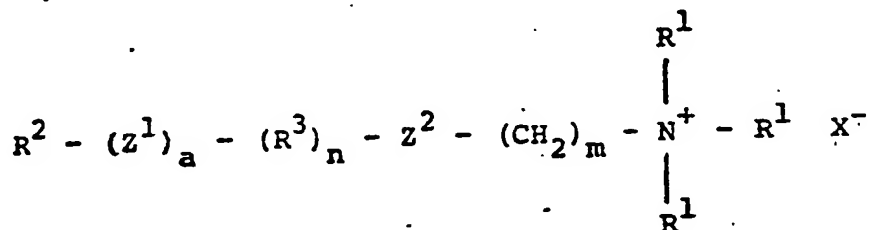


wherein R₃ is selected from C₈ to C₂₀ alkyl, alkenyl and alkaryl groups; each R₄ is C₁₋₄ alkyl; n is from 1 to 6; and m is from 1 to 3.

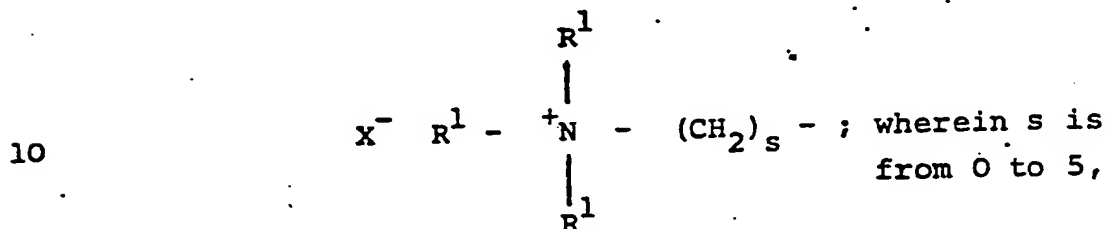
A specific example of a material in this group is:



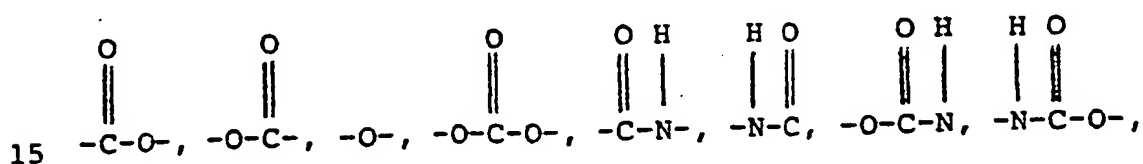
A further preferred type of cationic component, which is described in U.S. Patent Application Serial No. 811218 5 Letton, filed June 29th, 1977, and incorporated herein by reference, has the formula:



wherein R^1 is C_1 to C_4 alkyl; R^2 is C_5 to C_{30} straight or branched chain alkyl or alkenyl, alkyl benzene, or



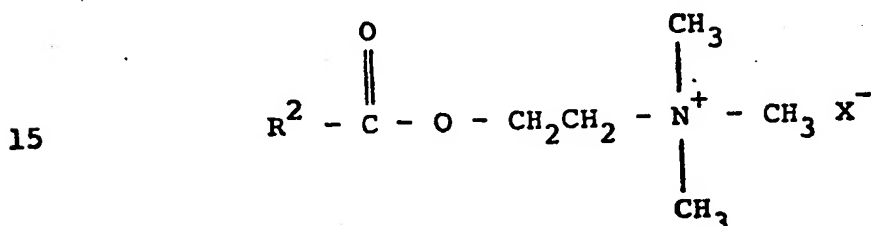
R^3 is C_1 to C_{20} alkyl or alkenyl; a is 0 or 1; n is 0 or 1; m is from 1 to 5; Z^1 and Z^2 are each selected from the group consisting of:



and wherein at least one of said groups is selected from the group consisting of ester, reverse ester, amide and reverse amide; and X is an anion which makes the compound water-soluble, preferably selected from the group consisting of halide, methyl sulfate, hydroxide, and nitrate, preferably chloride, bromide or iodine.

In addition to the advantages of the other cationic surfactants disclosed herein, this particular cationic component is environmentally desirable, since it is biodegradable, both in terms of its long alkyl chain and its nitrogen-containing segment.

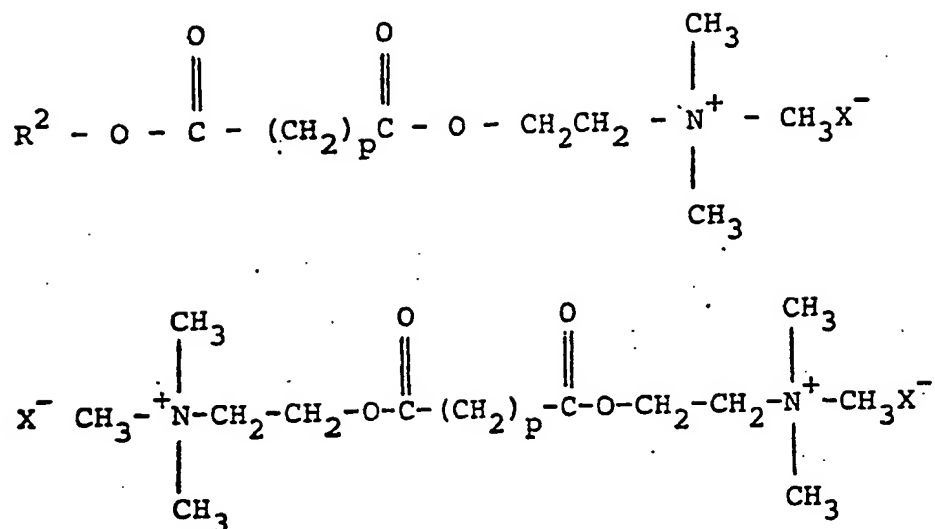
Particularly preferred cationic surfactants of this type are the choline ester derivatives having the following formula:



as well as those wherein the ester linkage in the above formula is replaced with a reverse ester, amide or reverse amide linkage.

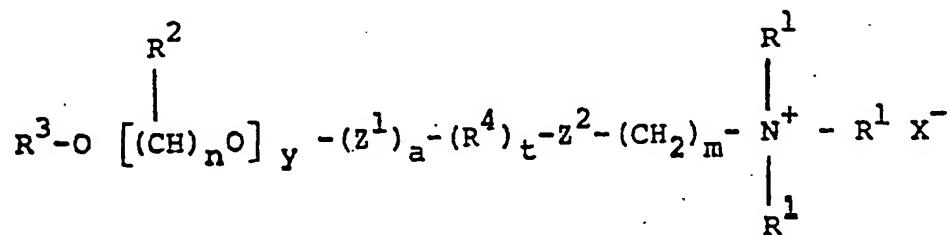
Particularly preferred examples of this type of cationic surfactant include caproyl choline ester quaternary ammonium halides ($\text{R}^2 = \text{C}_9$ alkyl), palmitoyl choline ester quaternary ammonium halides ($\text{R}^2 = \text{C}_{15}$ alkyl), myristoyl choline ester quaternary ammonium halides ($\text{R}^2 = \text{C}_{13}$ alkyl), lauroyl choline ester ammonium halides ($\text{R}^2 = \text{C}_{11}$ alkyl), and capryloyl choline ester quaternary ammonium halides ($\text{R}^2 = \text{C}_7$ alkyl).

Additional preferred cationic components of the choline ester variety are given by the structural formulas below, wherein p may be from 0 to 20.

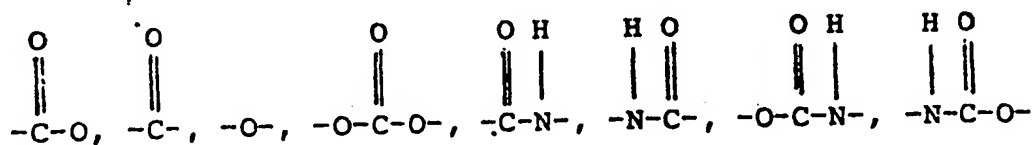


The preferred choline-derivative cationic substances, discussed above, may be prepared by the direct esterification of a fatty acid of the desired chain length with dimethylaminoethanol, in the presence of an acid catalyst. The reaction product is then quaternized with a methyl halide, forming the desired cationic material. The choline-derived cationic materials may also be prepared by the direct esterification of a long chain fatty acid of the desired chain length together with 2-haloethanol, in the presence of an acid catalyst material. The reaction product is then used to quaternize triethanolamine, forming the desired cationic component.

Another type of novel particularly preferred cationic material, described in U.S. Patent Application Serial No. 811219 Letton, filed June 29, 1977 and incorporated herein by reference, are those having the formula:



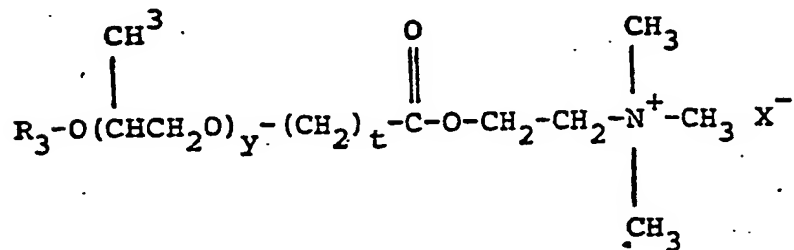
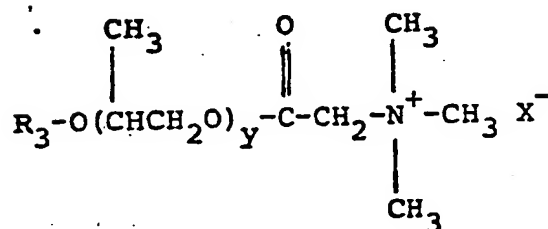
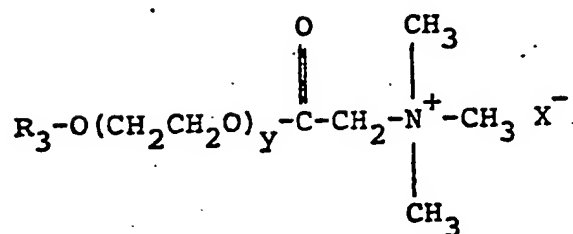
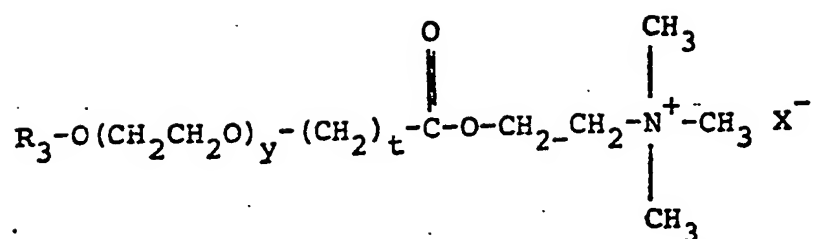
In the above formula, each R^1 is a C_1 to C_4 alkyl group, preferably a methyl group. Each R^2 is either hydrogen or C_1 to C_3 alkyl, preferably hydrogen. R^3 is a C_4 to C_{30} straight or branched chain alkyl, alkenyl, or alkyl benzyl group, preferably a C_8 to C_{18} alkyl group, most preferably a C_{12} alkyl group. R^4 is a C_1 to C_{10} alkylene or alkenylene group. n is from 2 to 4, preferably 2; y is from 1 to 20, preferably from about 1 to 10, most preferably about 7; a may be 0 or 1; t may be 0 or 1; and m is from 1 to 5, preferably 2. z^1 and z^2 are each selected from the group consisting of:



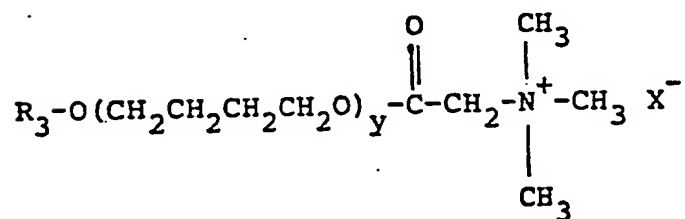
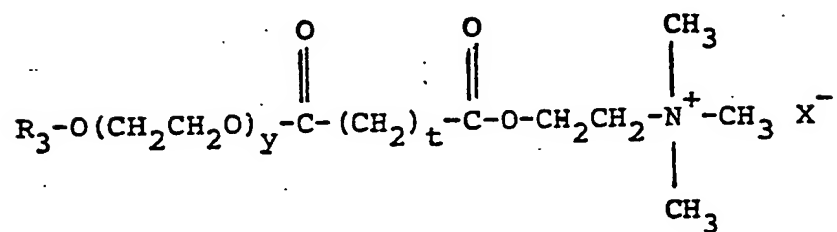
and wherein at least one of said groups is selected from the group consisting of ester, reverse ester, amide and reverse amide. X is an anion which will make the compound water-soluble and is selected from the group consisting of halides, methylsulfate, hydroxide and nitrate, particularly chloride, bromide and iodide.

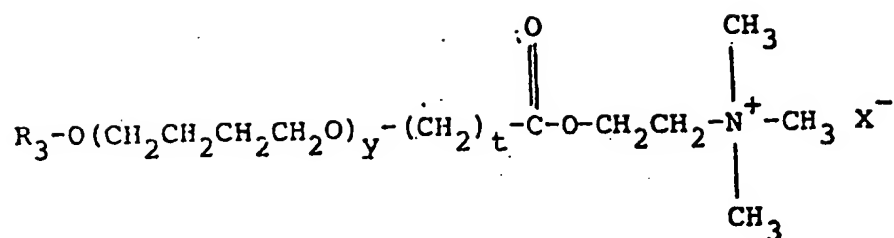
These surfactants, when used in the compositions of the present invention, yield excellent particulate soil, body soil, and grease and oil soil removal. In addition, the detergent compositions control static and soften the fabrics laundered therewith, and inhibit the transfer of dyes in the washing solution. Further, these cationic surfactants are environmentally desirable, since both their long chain alkyl segments and their nitrogen segments are biodegradable.

Preferred embodiments of this type of cationic component are the choline esters (R^1 is a methyl group and z^2 is an ester or reverse ester group), particular formulas of which are given below in which t is 0 or 1 and y is from 1 to 20.



5





The preferred choline derivatives, described above, may be prepared by the reaction of a long chain alkyl polyalkoxy (preferably polyethoxy) carboxylate, having an alkyl chain of desired length, with oxalyl chloride, to form the corresponding acid chloride. The acid chloride is then reacted with dimethylaminoethanol to form the appropriate amine ester, which is then quaternized with a methyl halide to form the desired choline ester compound. Another way of preparing these compounds is by the direct esterification of the appropriate long chain ethoxylated carboxylic acid together with 2-haloethanol or dimethyl aminoethanol, in the presence of heat and an acid catalyst. The reaction product formed is then quaternized with methylhalide or used to quaternize trimethylamine to form the desired choline ester compounds.

As indicated above, the compositions of the invention comprise at least 50% by weight of the surfactant mixture of nonionic and/or water-soluble cationic surfactants. A highly preferred mixture of surfactants comprises by weight thereof

(i) at least 5%, preferably from 10 to 40% by weight of a cationic surfactant having the formula $R^1R^2R^3N^+A^-$ wherein R^1 represents a C_{6-24} alkyl or alkenyl group or C_{6-12} alkaryl group, each R^2 independently represents a $(C_nH_{2n}O)_xH$ group where n is 2, 3 or 4 and x is from 1 to 14, the sum total of $C_nH_{2n}O$ groups in R^2 being from 1 to 14, each R^3 independently represents a C_{1-12} alkyl or alkenyl group, an aryl group or a C_{1-6} alkaryl group, m is 1, 2 or 3, and A is an anion.

(ii) at least 30% by weight of a mixture of anionic and nonionic surfactants in a weight ratio from 7.5:1 to 1:100.

5 Mixtures of this sort are described in copending European Patent Application 78-200290.

Another highly preferred mixture of surfactants comprises 90%-99.5% by weight of an ethoxylated primary or secondary alcohol having from 9-15 carbon atoms in the alkyl group and containing from 4-9 ethylene oxide groups
10 per mole of alcohol and from 0.5%-10% of a water-soluble organic sulphate or sulphonate salt in which the organic group is a C₈₋₂₂ alkyl or alkaryl radicle.

In both these organic detergent systems, suitable anionic and nonionic surfactants are as described below.

15 The Anionic Surfactant

Water-soluble salts of the higher fatty acids, i.e. "soaps", can be used as the anionic detergent component of the compositions herein. This class of detergents includes ordinary alkali metal soaps such as the sodium,
20 potassium, ammonium and alkanolammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms and preferably from about 10 to about 20 carbon atoms. Soaps can be made by direct saponification of fats and soils or by the neutralization of free fatty acids.
25 Particularly useful are the sodium and potassium salts of the mixture of fatty acids derived from coconut oil and tallow, i.e. sodium or potassium tallow and coconut soap.

A highly preferred class of anionic detergents includes water-soluble salts, particularly the alkali metal, ammonium
30 and alkanolammonium salts, or organic sulfuric reaction products having in their molecular structure an alkyl or alkaryl group containing from about 8 to about 22, especially from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl"
35 is the alkyl portion of acyl groups). Examples of this

group of synthetic detergents which form part of the detergent compositions of the present invention are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_{8-18} carbon atoms) produced by reducing the glycerides of tallow or coconut oil and sodium and potassium alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branched chain configuration, e.g. those of the type described in USP 2,220, 099 and 2,477,383. Especially valuable are linear straight chain alkyl benzene sulfonates in which the average of the alkyl group is about 11.8 carbon atoms, abbreviated as $C_{11.8}$ LAS.

A preferred alkyl ether sulfate surfactant component of the present invention is a mixture of alkyl ether sulfates, said mixture having an average (arithmetic mean) carbon chain length within the range of about 12 to 16 carbon atoms, preferably from about 14 to 15 carbon atoms, and an average (arithmetic mean) degree of ethoxylation of from about 1 to 4 moles of ethylene oxide.

Other anionic detergent compounds herein include the sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; and sodium or potassium salts of alkyl phenol ethylene oxide ether sulfate containing about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl groups contain about 8 to about 12 carbon atoms.

Other useful anionic detergent compounds herein, include the water-soluble salts of esters of α -sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group, and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms

in the alkane moiety; alkyl ether sulfates containing from about 10 to 20 carbon atoms in the alkyl group and from about 1 to 30 moles of ethylene oxide; water-soluble salts of olefin sulfonates containing from about 12 to 24 carbon atoms; water-soluble salts of paraffin sulfonates containing from about 8 to 24, especially 14 to 18 carbon atoms, and β -alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Anionic surfactant mixtures can also be employed, for example 5:1 to 1:5 mixtures of an alkyl benzene sulfonate having from 9 to 15 carbon atoms in the alkyl radical and mixtures thereof, the cation being an alkali metal preferably sodium; and from about 2% to about 15% by weight of an alkyl ethoxy sulfate having from 10 to 20 carbon atoms in the alkyl radical and from 1 to 30 ethoxy groups and mixtures thereof, having an alkali metal cation, preferably sodium.

The Nonionic Surfactant

A water-soluble nonionic synthetic detergent is a further essential component of the instant compositions. Such nonionic detergent materials can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the polyoxyalkylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Examples of suitable nonionic detergents include:

1. The polyethylene oxide condensates of alkyl phenol, e.g. the condensation products of alkyl phenols having an alkyl group containing from 6 to 12 carbon atoms in either a straight chain or branched chain configuration,

- with ethylene oxide, the said ethylene oxide being present in amounts equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived, for example, from polymerised propylene, di-isobutylene, octene and nonene. Other examples include dodecylphenol condensed with 12 moles of ethylene oxide per mole of phenol; dinonylphenol condensed with 15 moles of ethylene oxide per mole of phenol; nonylphenol and di-iso-octylphenol condensed with 15 moles of ethylene oxide.
- 10 2. The condensation product of primary or secondary aliphatic alcohols having from 8 to 24 carbon atoms, in either straight chain or branched chain configuration, with from 1 to about 30 moles of alkylene oxide per mole of alcohol. Preferably, the aliphatic alcohol comprises
- 15 between 9 and 15 carbon atoms and is ethoxylated with between 2 and 12, desirably between 4 and 9 moles of ethylene oxide per mole of aliphatic alcohol. Such nonionic surfactants are preferred from the point of view of providing good to excellent detergency performance on fatty
- 20 and greasy soils, and in the presence of hardness sensitive anionic surfactants such as alkyl benzene sulfonates. The preferred surfactants are prepared from primary alcohols which are either linear (such as those derived from natural fats or, prepared by the Ziegler process from ethylene,
- 25 e.g. myristyl, cetyl, stearyl alcohols), or partly branched such as the Dobanols and Neodols which have about 25% 2-methyl branching (Dobanol and Neodol being Trade Names of Shell) or Synperonics, which are understood to have about 50% 2-methyl branching (Synperonic is a Trade Name of I.C.I.)
- 30 or the primary alcohols having more than 50% branched chain structure sold under the Trade Name Lial by Liquichimica. Specific examples of nonionic surfactants falling within the scope of the invention include Dobanol 45-4, Dobanol 45-7, Dobanol 45-11, Dobanol 91-3, Dobanol 91-6, Dobanol 91-8,
- 35 Synperonic 6, Synperonic 14, the condensation products of coconut alcohol with an average of between 5 and 12 moles

of ethylene oxide per mole of alcohol, the coconut alkyl portion having from 10 to 14 carbon atoms, and the condensation products of tallow alcohol with an average of between 7 and 12 moles of ethylene oxide per mole of alcohol, the
5 tallow portion comprising essentially between 16 and 22 carbon atoms. Secondary linear alkyl ethoxylates are also suitable in the present compositions, especially those ethoxylates of the Tergitol series having from about 9 to 16 carbon atoms in the alkyl group and up to about 11,
10 especially from about 3 to 9, ethoxy residues per molecule. 3. The compounds formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The molecular weight of the hydrophobic portion generally falls in the range of about
15 1500 to 1800. Such synthetic nonionic detergents are available on the market under the Trade Name of "Pluronic" supplied by Wyandotte Chemicals Corporation.

Detergency Builders

The compositions of the invention also contain from 10%
20 to 96.9% of detergency builders, preferably from 20 to 60% thereof.

Suitable detergent builder salts useful herein can be of the polyvalent inorganic and polyvalent organic types, or mixtures thereof. Non-limiting examples of suitable water-
25 soluble, inorganic alkaline detergent builder salts include the alkali metal carbonates, borates, phosphates, polyphosphates, tripolyphosphates, bicarbonates and sulfates.

Examples of suitable organic alkaline detergency builder salts are:

- 30 (1) water-soluble amino polyacetates, e.g., sodium and potassium ethylenediaminetetraacetates, nitrilotriacetates, and N-(2-hydroxyethyl)nitrilodiacetates;
- (2) water-soluble salts of phytic acid, e.g., sodium and potassium phytates;
- 35 (3) water-soluble polyphosphonates, including, sodium, potassium and lithium salts of ethane-1-hydroxy-1,1-diphosphonic acid; sodium, potassium and lithium salts of methylenediphosphonic acid and the like.

(4) water-soluble polycarboxylates such as the salts of lactic acid, glycollic acid and ether derivatives thereof as disclosed in Belgian Patents 821,368, 821,369 and 821,370; succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid; citric acid; aconitic acid, citraconic acid, carboxymethyloxysuccinic acid, lactoxysuccinic acid, and 2-oxa-1,1,3-propane tricarboxylic acid; oxydisuccinic acid, 1,1,2,2-ethane tetracarboxylic acid, 1,1,3,3-propane tetracarboxylic acid and 1,1,2,3-propane tetracarboxylic acid; cyclopentane-cis, cis, cis-tetracarboxylic acid, cyclopentadienide pentacarboxylic acid, 2,3,4,5-tetrahydrofuran-cis, cis, cis-tetracarboxylic acid, 2,5-tetrahydrofuran-cis-dicarboxylic acid, 1,2,3,4,5,6-hexane-hexacarboxylic acid, mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent 1,425,343.

Mixtures of organic and/or inorganic builders can be used herein. One such mixture of builders is disclosed in Canadian Patent No. 755,038, e.g. a ternary mixture of sodium tripolyphosphate, trisodium nitrilotriacetate, and trisodium ethane-1-hydroxy-1,1-diphosphonate.

A further class of builder salts is the insoluble alumino silicate type which functions by cation exchange to remove polyvalent mineral hardness and heavy metal ions from solution. A preferred builder of this type has the formulation $\text{Na}_2(\text{AlO}_2)_z(\text{SiO}_2)_y \cdot x\text{H}_2\text{O}$ wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5 and x is an integer from about 15 to about 264. Compositions incorporating builder salts of this type form the subject of British Patent Specification No. 1,429,143 published March 24, 1976, German Patent Application No. OLS 2,433,485 published February 6, 1975, and OLS 2,525,778 published January 2, 1976, the disclosures of which are incorporated herein by reference.

Another type of detergency builder material useful in the present compositions and processes comprises a water-soluble material capable of forming a water-insoluble reaction product with water hardness cations preferably in combination with a crystallization seed which is capable of providing growth sites for said reaction product. Such "seeded builder" compositions are fully disclosed in British Patent Specification No. 1,424,406.

Suds Control System

The suds suppressing system consists of a mixture of wax, hydrophilic nonionic dispersant and hydrophobic silica in the proportions discussed hereinbefore. Preferably it contains from 60% to 85% of wax, from 5% to 15% of dispersant and from 5% to 15% of silica. Silicones should preferably be absent as they tend to cause suds suppression in hand wash conditions.

Wax

Preferred waxes are petroleum waxes of the micro-crystalline type, melting generally in the temperature range from 35°C to 110°C. Paraffin waxes may also be used, but preferred hydrocarbon wax mixtures comprise not more than 70% paraffin wax. Suitable micro-crystalline waxes include Shell micro-crystalline wax - HMP, and -W4, and micro-crystalline waxes sold by Witco, and many other suppliers. Paraffin waxes are widely commercially available. Other suitable waxes include Fischer-Tropsch and oxidised Fischer-Tropsch waxes, ozokerite, ceresin, montan wax, beeswax, candelilla, and carnauba wax, and spermacetti, and other ester waxes having a saponification value less than 100. Other waxy materials which may be employed, preferably constituting less than 50% of the wax component, are partial esters of polyhydric alcohols such as C₁₂ to C₂₀ acid esters of glycerol and sorbitan. Glycerol monostearate is a preferred member of this class. Mixtures of these waxes and waxy materials may be employed.

As indicated above, an important consideration in selecting the wax for any given realization of the invention, is its melting point in so far as this controls the softening point of the suds suppressing system as a whole.

The Dispersing Agent

The dispersing agent is a hydrophilic nonionic surfactant having a hydrophilic-lipophilic balance (HLB) in the range from 14 to 19. These substances are too hydrophilic to function effectively as organic detergent components. Many nonionic surfactants having HLB in the above range are known, and a list is given in McCutcheons Detergents and Emulsifiers, North American Edition, 1977 - pages 22-26. Preferred nonionic surfactants for this purpose are relatively highly ethoxylated alcohols and alkyl phenols. Preferred are ethoxylated C_{12} to C_{20} , preferably C_{16} to C_{18} , alcohols with 15 to 100 preferably 20 to 80 ethoxy groups per molecule. The alcohol portion may be branched or unbranched, primary or secondary. Tallow alcohol ethoxylates are most preferred.

Silica

Another essential component in the suds controlling system is a hydrophobic silica. Suitable silicas are microfine, hydrophobic, particulate silicas. These silicas usually have an average primary particle diameter from about 5 millimicrons ($m\mu$) to about 100 $m\mu$, preferably from 10 $m\mu$ to 30 $m\mu$. The primary particles can form aggregates -- frequently termed secondary particles -- having frequently an average particle diameter in the range from about 0.3 μ to about 3 μ . Suitable silica components can additionally be characterized by a specific surface area from about 50 m^2/g to about 400 m^2/g , preferably from 100 m^2/g to 200 m^2/g . The specific surface area can be determined with the aid of the N_2 -adsorption method. The preferred silica component herein can additionally be defined in having a pH in the range from 6 to 12, to thus be better compatible with the usually

alkaline laundry solution. Generally preferred herein are precipitated hydrophobic microfine silicas with preferred species commercially available under the Trade Names QUSO WR82 and QUSO WR50 from Philadelphia Quartz Company.

- 5 Additional examples of suitable silicas herein can include pyrogenic silica and aerogel and xerogel silicas provided their general physical properties are as set forth above. The silica can be rendered hydrophobic through one of the well-known treatments such as e.g. disclosed in U.S. Patent
10 3,207,698.

Whilst the mechanism of operation of the suds suppression system is not fully understood, it appears that the system has little or no suds suppressing effect at temperatures below its softening point. At about the
15 softening point, which is that of the wax-dispersant mixture, the mixture disperses in the wash liquor, the dispersion being aided by the dispersing agent, and the mixture then acts as a suds suppressant. If the softening point is suitably chosen, as by selection of wax and the
20 dispersant and the proportions of each, little or no depression of hand wash suds is caused. In a drum washing machine, suds tend to increase continuously as the temperature of the wash liquor increases. This increase in suds can be reversed at a chosen temperature by choosing, once
25 again, the temperature at which the suds controlling system softens. For most practical purposes, the softening point is in the range from about 40°C to about 70°C, preferably about 50°C.

The softening point can be determined by warming a
30 sample of wax or the mixture in the hot stage of a microscope and observing the temperature at which the crystal structure of the wax begins to break down to a substantial degree.

Additional Components

The compositions of the present invention can be supplemented by all manner of detergent components, either by including such components in the aqueous slurry to be dried or by admixing such components with the compositions of the invention following the drying step. Soil-suspending agents at about 0.1% to 10% by weight such as water-soluble salts of carboxymethyl-cellulose, carboxyhydroxymethyl cellulose, and polyethylene glycols having a molecular weight of about 400 to 10,000 are common components of the present invention. Dyes, pigment optical brighteners, and perfumes can be added in varying amounts as desired.

Other materials such as fluorescers, enzymes in minor amounts, anti-caking agents such as sodium sulfo-succinate, and sodium benzoate can also be added. Enzymes suitable for use herein include those discussed in U.S. Patents 3,519,570 and 3,533,139 to McCarty and McCarty et al issued July 7, 1970 and January 5, 1971, respectively.

Anionic fluorescent brightening agents are well-known materials, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-anilino-s-triazin-6-ylamino)stilbene-2:2'-disulphonate, disodium 4,4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylaminostilbene-2:2'-disulphonate, disodium 4,4'-bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2:2'-disulphonate, disodium 4,4'-bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2'-disulphonate, disodium 4,4'-bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2'-disulphonate, disodium 4,4'-bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2'-disulphonate and sodium 2(stilbyl-4''-(naphtho-1', 2', 3'-1,2,3-triazole-2''-sulphonate.

An alkali metal, or alkaline earth metal, silicate can also be present. The alkali metal silicate preferably is present in an amount from 0.5% to 10% preferably from 3% to 8%. Suitable silicate solids have a molar ratio of $\text{SiO}_2/\text{alkali metal}_2\text{O}$ in the range from about 0.5 to about 4.0, but much more preferably from 1.0 to 1.8, especially about 1.6. The

alkali metal silicates suitable herein can be commercial preparations of the combination of silicon dioxide and alkali metal oxide, fused together in varying proportions.

Preparing The Composition

5 The granular detergent compositions of the invention may be prepared in any effective way, for instance by granulating techniques. Generally, a spray dried base powder is prepared containing some or all of the non-heat sensitive components, and the other components are added to
10 it, by dry blending or spray on or like means as appropriate. Thus the anionic and nonionic surfactants and the builder and filler components can be spray dried in conventional manner to form a base powder composition and the cationic
15 component can then be added to the base powder either as an approximately 1:1 mixture with part of the builder or filler components retained for that purpose, or as an inclusion complex of, for instance, urea. Alternatively, the cationic
20 surfactant can be sprayed onto the base powder, or added as a dry mixed prill agglomerated with an inorganic or organic agglomerating aid, or can be separately spray dried and
25 added to the base powder as a dry mixed granule. Alternatively, the cationic surfactant and base powder compositions can be individually spray dried in separate stages of a multi-stage spray drying tower.

25 Generally, in view of the known problems associated with spray drying mixtures containing polyethoxy nonionic detergents, the spray dried base powder contains the anionic and cationic detergents, builders etc., and the nonionic surfactant is sprayed onto the base powder.

A critical feature of the present invention is that the suds-controlling system must be present as a uniform dispersion and be in admixture with preformed granules comprising some or all of the organic detergent and/or detergency builder components of the composition. That is to say, the suds-controlling system is prepared in the form of a premix by intimately mixing the dispersing agent, silica and wax, and the suds-suppressor premix is then added to a granular base composition comprising organic detergent and/or detergency builder. Preferably, the suds controlling system is prepared by melting together the wax and the dispersing agent and raising the temperature to at least that at which they form a single phase, dispersing the silica in the mixture by suitable mixing means, and cooling the mixture rapidly so that the separation does not take place before the mixture freezes. Optionally, a small amount of an emulsifier may be added to or included in the wax to inhibit phase separation of the wax and the hydrophilic dispersant during cooling of the molten mixture. Suitable emulsifiers are nonionic surfactants of low HLB viz less than about 6, e.g. glycerine monostearate and like substances. Cooling may be performed by spray cooling or by cooling a film of the melt on chilling rolls, or by like methods. Alternatively, the fluid dispersion may be sprayed onto the cool spray dried base powder or onto a particulate carrier which is then dry mixed with base powder and forms part of the detergent composition. Preferably, if the nonionic detergent has been or is to be sprayed onto the base powder, the suds controlling system is preformed in particulate form, either alone or on a particulate carrier.

EXAMPLE I

A spray dried detergent base powder was prepared containing the following ingredients, in parts by weight.

7.4%	anionic	Sodium dodecylbenzene sulphonate	3.4 parts	$\frac{3.4}{103.4}$ 3%
		C ₁₂₋₁₄ alkyl methyl dihydroxyethyl ammonium chloride.	1.7 parts	
5	cationic	Dobanol 45-7 ⁽¹⁾	0.75 "	
		Sodium tripolyphosphate	33.0 "	
		Sodium sulphate	23.0 "	
		Sodium silicate (Na ₂ O:SiO ₂ 1.6)	5.0 "	
10		Sodium carboxymethyl cellulose	0.8 "	
		Sodium ethylene diamine tetra methylene phosphonate	0.5 "	
		Sodium ethylene diamine tetraacetate	0.2 "	
		Optical brightener .	0.2 "	
15		Water and miscellaneous impurities	13.2 "	

To the spray dried base powder was sprayed on:

Dobanol 45-7 ⁽¹⁾	3.25 parts
Perfume	0.2 parts

The resulting granular product was dry mixed with, in parts by weight:-

Sodium perborate tetrahydrate	12.0 parts
Enzyme-containing powder	1.3 parts
Suds controlling system	1.5 parts
to provide 100 parts of a detergent composition according to the invention.	

(1) Trade Name. Primary C₁₄₋₁₅ alcohols condensed with 7 molar proportions of ethylene oxide.

The suds controlling system contained, by weight:

Shell Microcrystalline Wax W4 ⁽²⁾	1.16 parts
Tallow alcohol condensed with 25 molar proportions of ethylene oxide	0.17 parts
Hydrophobic silica ⁽³⁾	0.17 parts

(2) Trade Name

(3) QUSO 82 - Trade Name Philadelphia Quartz Company.

10 This had been prepared by melting together the wax and the ethoxylated tallow alcohol at 95°C, and mixing into the so-formed single phase liquid the hydrophobic silica, employing a high shear mixer. The dispersion was then spray cooled to form granules.

15 The product was used at 0.5% concentration in a wash liquor for hand washing clothes at 40°C, and formed copious suds. The product was also used in a wash liquor at 0.75% concentration in the boil wash cycle of a Miele domestic washing machine. A small amount of suds developed as the wash temperature rose to about 50°C, and the level of suds thereafter decreased slightly as the temperature rose to the wash temperature (95°C). Corresponding
20 product lacking the suds controlling system gave equal suds in the hand wash but over-sudsed in the machine wash.

Similar results are obtained if in the organic detergent mixture the 3.4 parts of sodium dodecylbenzene sulphate are replaced by 1.7 parts of the same and 1.7
25 parts of sodium tallow alkyl sulphate, or if the Dobanol 45-7 is replaced by Dobanol 45-4, coconut alcohol condensed with 6 molar proportions of ethylene oxide, or tallow alcohol condensed with 9 to 11 molar proportions
30 of ethylene oxide.

Similar results are obtained if the 33 parts of sodium tripolyphosphate are replaced by 3 parts of the same and 30 parts of Zeolite A.

Similar results are obtained when the suds controlling system is replaced by uniform dispersions of the following compositions, in parts by weight:-

	<u>System No.</u>	1	2	3	4
	(1) Shell Microcrystalline Wax (Congealing point 76°C)	-	5	-	-
5	(1) Shell Microcrystalline Wax (Congealing point 85°C min.)	7.0	-	8.8	8.2
	Tallow ethoxylate (moles ethylene oxide per mole tallow alcohol)	1.1(25)	2(80)	0.6(25)	0.9(12)
10	(2) QUSO-82	1.1	3	0.6	0.9
	Glycerine monostearate	0.8	-	-	-
	(1) Trade Name. Congealing point determined by test ASTM - D938.				
15	(2) Philadelphia Quartz. Ultra fine hydrophobic silica.				

EXAMPLE II

20 A spray dried detergent base powder was prepared
containing the following ingredients, in parts by weight:-

	Sodium dodecylbenzene sulphonate	1 part
	Sodium tripolyphosphate	33 parts
	Sodium carboxymethyl cellulose	1.4 parts
	Sodium silicate ($\text{SiO}_2:\text{Na}_2\text{O}$ 2.0)	5 parts
25	Sodium sulphate	20 parts
	Sodium ethylene diamine tetra methylene phosphonate	0.5 parts
	Sodium ethylene diamine tetraacetate	0.2 parts
	Optical brightener	0.2 parts
30	Water and miscellaneous impurities	11.7 parts

To the resultant granular base powder was sprayed
on:-

Dobanol 45-7 (as in Example I)	12.0 parts
Perfume	0.2 parts

The resulting granular product was dry mixed with, in parts by weight:-

	Sodium perborate tetrahydrate	12.0 parts
	Enzyme containing powder	1.3 parts
5	Suds controlling system	1.5 parts

to provide 100 parts of a detergent composition according to the invention. The suds controlling system was as in Example 1.

When used as in Example 1, this composition provided adequate suds in hand washing conditions and acceptable freedom from oversudsing in the boil wash cycle of a domestic washing machine. Corresponding product wherein the above suds controlling system was replaced by an equal weight of powdered microcrystalline wax oversudsed in the machine wash.

EXAMPLE III

A granular detergent composition is prepared substantially as described in Example I consisting of, per cent by weight:-

		%
20	Sodium dodecylbenzene sulphonate	5.0
	Tallow alkyl trimethyl ammonium chloride	5.0
	Tallow alcohol condensed with 11 molar proportions of ethylene oxide	5.0
25	Dobanol 45-4	5.0
	Sodium tripolyphosphate	20.0
	Sodium silicate ($\text{SiO}_2\text{Na}_2\text{O}$ 2.0)	8.0
	Sodium sulphate	19.3
30	Sodium carboxymethyl cellulose	1.0
	Sodium ethylene diamine tetraacetate	0.3
	Sodium perborate tetrahydrate	20.0
	Optical brightener	0.3
	Perfume	0.1
35	Suds controlling system	3.0
	Water and miscellaneous	<u>8.0</u>

This composition provides good sudsing in hand wash conditions and does not over-suds in a drum type automatic washing machine even in the 95°C wash cycle.

CLAIMS

1. A granular built detergent composition having a controlled sudsing pattern characterised by:-

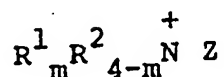
- 5 (A) from 3% to 30% of organic detergent containing at least 50% by weight thereof of nonionic and/or water-soluble cationic surfactant;
- (B) from 10% to 96.9% of detergency builder; and
- 10 (C) as suds controlling system, from 0.1% to 5% of a uniform dispersion containing by weight thereof
- (a) from 5% to 50% of a hydrophilic nonionic dispersing agent having an HLB range in the range from 14 to 19,
- (b) from 5% to 55% of hydrophobic silica, and
- (c) from 40% to 90% of wax;

15 wherein the suds-controlling system is in admixture with preformed granules comprising some or all of the organic detergent and/or detergency builder components of the composition.

2. A composition according to Claim 1 wherein the organic detergent contains from 35% to 99% of nonionic detergent.

- 20 3. A composition according to Claim 1 wherein the organic detergent component (A) comprises a water soluble or water dispersible combination of ethoxylated nonionic, water-soluble quaternary ammonium cationic, and anionic surfactants wherein the weight ratio of anionic to cationic surfactant
- 25 is no more than 5:1 and the weight ratio of nonionic to cationic surfactant is at least 2:3 and wherein the surfactant system contains anionic and cationic surfactants in an equivalent ratio of at least 1:1.

4. A composition according to Claim 3 wherein the cationic surfactant has the general formula:



- 5 wherein R^1 is selected from C_8 - C_{20} alkyl, alkenyl and alkaryl groups; R^2 is selected from C_1 - C_4 alkyl and benzyl groups; Z is anion in number to give electrical neutrality; and m is 1, 2 or 3; provided that when m is 2, R^1 has less than 15 carbon atoms and when m is 3, R^1 has less than 9 carbon atoms.
- 10 5. A composition according to any of Claims 1 to 4 wherein the organic detergent component comprises, by weight thereof,
- (i) at least 5% preferably from 10% to 40% by weight of a cationic surfactant having the general formula $R^1 R^2_m R^3_{3-m} N^+ A$ wherein R^1 represents a C_6 - C_{24} alkyl or alkenyl group or a C_6 - C_{12} alkaryl group, each R^2 independently represents a $(C_n H_{2n} O)_x$ group where n is 2, 3 or 4 and x is from 1 to 14, the sum total of $C_n H_{2n} O$ groups in R^2_m being from 1 to 14, each R^3 independently represents a C_1 - C_{12} alkyl or alkenyl group, aryl group or a C_1 - C_6 alkaryl group, m is 1, 2 or 3, and A is an anion
- 15 20 (ii) at least 30% by weight of a mixture of anionic and nonionic surfactants in a weight ratio from 7.5:1 to 1:100.
- 25 6. A composition according to Claim 5 wherein the cationic surfactant has the formula:



- wherein R^1 represents a C_8 - C_{18} alkyl or alkenyl group or a C_6 - C_{12} alkaryl group, n is 2 or 3, and m is from 1, 2 or 3.
- 30

7. A composition according to any one of Claims 3 to 6 wherein the weight ratio of anionic to nonionic surfactant is in the range from 1:1 to 1:10, the weight ratio of anionic to cationic surfactant is in the range from 2:1 to 1:2 and the weight ratio of nonionic to cationic surfactant is in the range from 4:1 to 3:2.
8. A composition according to any one of the previous Claims wherein the suds controlling system has a melting point in the range from 40°C to 70°C.
9. A composition according to any one of the previous Claims wherein the wax component of the suds controlling system comprises microcrystalline hydrocarbon wax optionally admixed with up to 70% by weight of the mixture of paraffin wax.
10. A composition according to any one of the previous Claims wherein the dispersing agent of the suds controlling system is an ethoxylated C₁₂-C₂₀ fatty alcohol or an ethoxylated alkyl phenol having from 8 to 16 carbon atoms in the alkyl group, having from 15 to 100 ethylene oxide groups in the molecule.



European Patent
Office

EUROPEAN SEARCH REPORT

0008829

Application number

EP 79 200 471.5

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. CL)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	<p><u>FR - A2 - 2 264 086 (PROCTER & GAMBLE)</u> * claims 1 to 3 and 7; page 1, line 38 to page 2, line 2; page 2, lines 22 to 28; page 8, lines 19 to 36; page 11, example 1 *</p> <p>--</p> <p><u>FR - A - 2 231 745 (HENKEL)</u> * claims 1 and 4; page 3, lines 9 to 19; page 6, lines 12 to 35; page 11, lines 10 to 18 *</p> <p>--</p> <p><u>AT - E - 2 67 024 (UNILEVER)</u> * claims 11 and 13; page 3, lines 39 to 45; page 4, lines 3 to 6; page 8, table 3 *</p> <p>--</p>	<p>1-3, 8-10</p> <p>1,3,10</p> <p>1,10</p>	<p>C 11 D 1/86 C 11 D 1/38 C 11 D 1/68</p> <p>TECHNICAL FIELDS SEARCHED (Int. CL)</p> <p>C 11 D 1/00</p>
A	<p><u>FR - A - 2 231 743 (HENKEL)</u> * complete document *</p> <p>--</p>		
A	<p><u>DE - A - 2 124 526 (PROCTER & GAMBLE)</u> * complete document *</p> <p>--</p>		
A	<p><u>FR - A1 - 2 380 340 (BASF)</u> * complete document *</p> <p>----</p>		
<p>The present search report has been drawn up for all claims</p>			<p>δ: member of the same patent family, corresponding document</p>
Place of search		Date of completion of the search	Examiner
Berlin		15-11-1979	SCHULTZE

